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**ADP014257**

**TITLE:** Biodegradable Polyester/Layered Silicate Nanocomposites

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This paper is part of the following report:

**TITLE:** Materials Research Society Symposium Proceedings Volume 740  
Held in Boston, Massachusetts on December 2-6, 2002. Nanomaterials for  
Structural Applications

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## Biodegradable Polyester / Layered Silicate Nanocomposites

Pralay Maiti<sup>1</sup>, Carl A. Batt<sup>2</sup> and Emmanuel P. Giannelis<sup>1</sup>

<sup>1</sup>Department of Material Science and Engineering, <sup>2</sup>Department of Food Science, Cornell University Ithaca, NY 14853, U.S.A.

### ABSTRACT

Nanocomposites of  $\alpha$ -hydroxy polyester, polylactide (PLA) and  $\beta$ -hydroxy polyester, polyhydroxybutyrate (PHB) with layered silicates have been successfully prepared by melt extrusion of PLA and PHB with organically modified montmorillonite (MMT) and fluoromica. The mechanical properties of the nanocomposites are improved compared to the neat polymers. Storage modulus increase up to 40% compared with the pure polymers by adding only 2-3 wt% nanoclay. Biodegradation can be controlled by the choice of the nanoclay used.

### INTRODUCTION

Concerns over the persistence of plastics in the environment, shortage of landfill space, increased cost of solid waste disposal, emissions during incineration, and negative impact on wildlife through ingestion and entrapment have increased research and development efforts on biodegradable polymers. The challenge remains to design biodegradable alternatives to conventional plastics that combine the mechanical and physical properties of the latter, yet they are susceptible to microbial and environmental degradation without adverse effect on the environment. Improvements in biodegradability typically, however, come at the expense of performance and trade-offs often need to be made in achieving performance while maintaining biodegradation.

Recently, polylactides (PLA) and polyhydroxybutyrate (PHB) have received much research attention as biodegradable polymers [1-4]. However, their strength as well as thermal stability, gas barrier, and solvent and flame resistance are not sufficient for end use. Polymer nanocomposites made by incorporating inorganic nanoparticles such as nanoclays into a polymer matrix have been shown to improve materials properties. In addition, the nanocomposites can avoid trade-offs in materials properties and, thus, design materials with a unique set of properties that cannot be realized in conventional filled polymers and composites.

A typical challenge in synthesizing polymer nanocomposites is the inherent incompatibility between the polymer matrix and the inorganic nanoparticles. To circumvent this problem the nanoparticles are organically modified. For example, nanoclays can be ion-exchanged with different alkyl ammonium or phosphonium ions to render them organophilic and, thus, more compatible with the polymer [5-9].

In this paper we report the synthesis and properties of both PLA and PHB nanocomposites with different nanoclays prepared by melt intercalation. The microstructure, mechanical properties and biodegradability are presented and discussed.

## EXPERIMENTAL

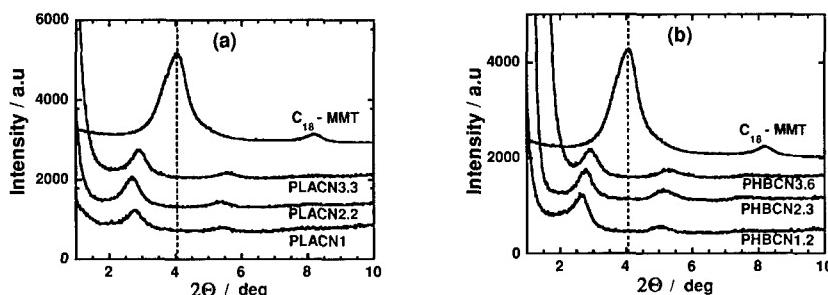
Polylactide (PLA) ( $M_w = 1.87 \times 10^5$ ,  $M_w/M_n = 1.76$  and D-content = 1.1-1.7%) was supplied by Dow Cargil Company and dried under vacuum at 80°C before use. Montmorillonite (MMT) and fluoromica (dimethyl dialkyl ammonium, MAE, and dipolyoxyethylene alkyl ammonium, MEE) were used as received. Nanocomposites were prepared by melt extrusion using a twin screw, bench top microextruder operated at 190°C. The extruded and pelletized strands were dried under vacuum at 80°C to remove residual water. The inorganic content was measured by measuring the residue after heating at 950°C in a furnace. The numbers in the nanocomposite sample notation represent the percent nanoclay content. Unless otherwise specified the nanocomposites are based on  $C_{18}$ -MMT.

X-ray diffraction experiments were performed using a  $\theta$ - $\theta$  diffractometer (Scintag) equipped with a germanium detector using  $CuK\alpha$  radiation and a graphite monochromator (wavelength,  $\lambda = 0.154$  nm). The generator was operated at 45 kV and 40 mA. Dynamic mechanical measurements were performed using  $15 \times 4 \times 1.5$  mm<sup>3</sup> samples on a TA Instrument (DMA 2980) in tension. The temperature was ranged from -50 to 150°C using a heating rate of 2°C/min. Biodegradation experiments were performed by measuring the weight loss of  $2 \times 2 \times 0.5$  mm<sup>3</sup> sheets immersed in compost manure at 60°C and 90% humidity in a closed chamber.

## RESULTS AND DISCUSSION

### Microstructure

Wide angle X-ray diffraction (WAXD) patterns of the nanocomposites based on octadecyl ammonium exchanged montmorillonite are shown in Figure 1. The peak position of the nanocomposites shifted towards a lower diffraction angle when compared to the base nanoclay suggesting that spacing of the silicate layers increases by intercalation of polymer chains in the galleries. A small decrease in d-spacing with increasing silicate content is also seen.



**Figure 1.** WAXD patterns of PLA (left) and PHB (right) nanocomposites. The pattern of the base nanoclay is included for comparison. The numbers on the sample notation indicate the percent inorganic content in the nanocomposite.

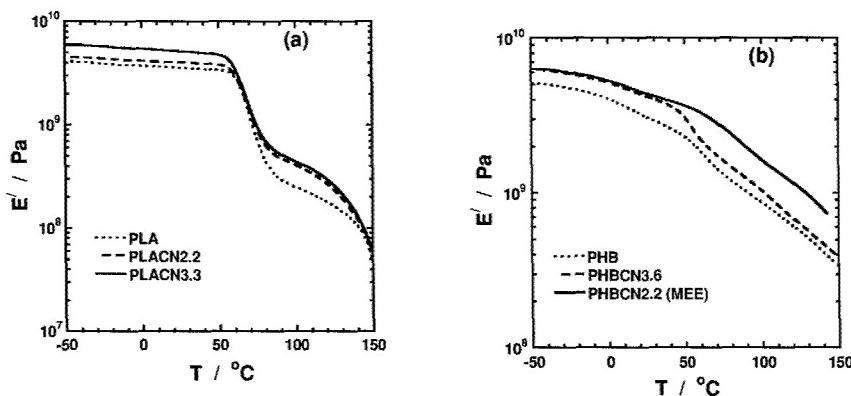
The peaks in the X-ray diffraction patterns are evidence of intercalated nanocomposites in which the spacing increases as a result of polymer intercalation while the regular stacking of the silicate layers is maintained. Transmission electron microscopy also reveals the presence of intercalated nanocomposites in agreement with the X-ray diffraction experiments. The nanocomposites based on fluoromica show similar behavior.

### **Dynamic Mechanical Property**

The storage modulus of PLA and PHB nanocomposite as a function of temperature is shown in Figure 2. The modulus,  $E'$ , increases with increasing nanoclay content in both systems. The storage modulus at 20 °C and percent increment with respect to the pure polymers are summarized in Table I. In general for the same amount of nanoclay the fluoromicas lead to higher increases in modulus compared to montmorillonite. The nanocomposites show about a 40% increase with ~ 3 wt.% nanoclay. Another interesting feature lies in the temperature behavior of the two systems. At the glass transition temperature,  $T_g$ , the modulus decreases significantly, almost one order of magnitude, for PLA and its nanocomposites while a slight decrease is observed for PHB and its nanocomposites.

Using differential scanning calorimetry (DSC) we find that PHB is highly crystalline ( $\Delta H = 105 \text{ J/g}$ , ~70 % crystallinity [10]) while PLA shows only ~35% crystallinity ( $\Delta H = 35 \text{ J/g}$  [11]). The DSC study also shows that the crystallinity does not change in the nanocomposites compared to the neat polymer. We attribute the smaller decrease in modulus for PHB to the higher amount of crystallinity in that system.

The montmorillonite based nanocomposite exhibits a slightly lower  $T_g$  from the corresponding fluoromica and neat PHB. The lower  $T_g$  is due to the drop in molecular weight from 110K to 60 K in the montmorillonite based nanocomposite. No such degradation is observed for the fluoromica nanocomposite. The difference in behavior between the two nanoclays is probably due to their different surface chemistries (see below).



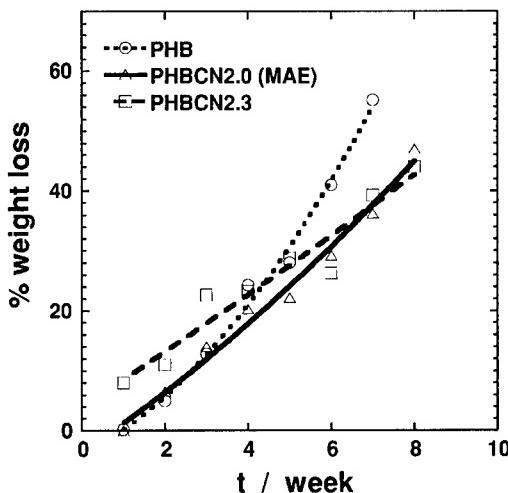
**Figure 2.** Storage modulus,  $E'$ , of samples annealed at 120 °C as a function of temperature (a) PLA (b) PHB system.

**Table I.** Storage Modulus of PLA and PHB Nanocomposites

System	E' / GPa at 20°C	% Increment w.r.t. PLA	System	E' / GPa at 20°C	% Increment w.r.t. PHB
PLA	3.63	-	PHB	3.25	-
PLACN1.0	4.00	10	PHBCN1.2	3.69	13
PLACN2.2	4.07	12	PHBCN2.3	4.00	23
PLACN3.3	5.26	44	PHBCN3.6	4.38	35
PLACN2.2(MAE)	3.55	no increment	PHBCN2.0(MAE)	4.31	33
PLACN2.1(MEE)	4.26	17	PHBCN2.2(MEE)	4.55	40

### Biodegradation in Compost Media

Figure 3 shows the weight loss of PHB and the corresponding nanocomposites as a function of time. Apparently, the degradation starts just after 1 week and at the initial stage the weight loss is almost the same for the pure PHB and the fluoromica based nanocomposite. But after 3 weeks of exposure the rate of degradation is much higher for the neat polymer compared to the nanocomposites. Interestingly, the montmorillonite based nanocomposite shows a higher initial



**Figure 3.** Percentage weight loss of PHB and its nanocomposite in the compost media at 60°C and 90% humidity as a function of degradation time.

decomposition rate compared even to the neat PHB. This is probably because of the presence of Al Lewis acid sites in the octahedral layers of montmorillonite and/or the presence of surface hydroxyl groups, which can catalyze the hydrolysis of the ester linkages in the polymer. Fluoromica contains Mg in the octahedral sites and much fewer surface hydroxyl groups. The decrease in polymer degradation after some point is attributed to the better barrier properties of the nanocomposites, which prevents oxygen and moisture from reaching the sample. Degradation occurs with the hydrolysis of ester linkages in the presence of moisture and subsequently weight loss appears from the consumption of oligomers by the microorganisms. The different mechanisms operating in the different systems are also evident in the surface roughening of the samples. Work is in progress to establish the degradation mechanism of polymer/silicate layer nanocomposites.

## CONCLUSIONS

PLA and PHB form well-ordered intercalated nanocomposites with organically modified silicates. The mechanical properties of the nanocomposites are improved compared to the neat polymers. Storage modulus increase up to 40% compared with the pure polymers by adding only 2-3 wt% nanoclay. Biodegradation can be controlled by the choice of the nanoclay used.

## ACKNOWLEDGEMENT

This work was supported by NASA and Rohm and Haas.

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